Available online at www.sciencedirect.com

ScienceDirect

Energy Procedia 63 (2014) 1827 – 1834

Energy Procedia

GHGT-12

Designer Amines for Post Combustion CO_2 Capture Processes

William Conway[a]*, Qi Yang[b], Susan James[b], Chiao-Chien Wei[a], Mark Bown[b], Paul Feron[a], and Graeme Puxty[a]

[a] *CSIRO Energy Flagship, Mayfield West NSW 2304 Australia*
[b] *CSIRO Manufacturing Flagship, Clayton VIC 3168 Australia*

Abstract

New amines with characteristics which counteract and contrast underlying issues with current solvents including chemical efficiency, chemical stability, and the ability to be operated over extended periods, will no doubt reduce the cost and environmental impact of CO_2 capture processes via their lower upfront investment in infrastructure and ongoing operational costs. Based on the superior absorption rate and performance of piperazine and the extended family of cyclic piperidine derivatives for CO_2 capture processes, a suite of structurally modified cyclic di-amine/tri-amine solvents utilizing the cyclic structure was proposed. The work presented here aims to provide higher efficiency solvents based on single molecule designer amines in comparison with MEA for post combustion capture of CO_2. This work details the comprehensive laboratory and modelling investigation of the structurally modified amines series for CO_2 capture processes and a comparison to the capture performance of monoethanolamine (MEA). Thirty designer amines have been synthesised here and their CO_2 cyclic capacities measured using quantitative ^{13}C NMR spectroscopy. Cyclic capacity results indicated the majority of the designer amines showed improved cyclic capacity (when expressed on molar or mass ratios) compared to MEA. Twelve amines achieved greater than 80% improvement in cyclic capacity over MEA (expressed as moles of CO_2/mol of nitrogen) with the largest improvement achieving a 158% increase. Estimations of the energy requirements for CO_2 capture for each of the amines was performed here. Ten of the amines synthesised here demonstrated improvements of 27% or greater than the energy performance of MEA, with the largest improvement being 32%. Following this, a selection of designer amines was progressively synthesized at larger scales allowing measurements of CO_2 absorption rates using a wetted wall column at 40°C. Comparable mass transfer rates were observed for two amines, which in combination with the cyclic capacity data and energy estimates places them firmly as promising candidates for CO_2 capture.

Peer-review under responsibility of the Organizing Committee of GHGT-12

* Corresponding author. Tel.: +61 2 49 606098
E-mail address: will.conway@csiro.au

Peer-review under responsibility of the Organizing Committee of GHGT-12
doi:10.1016/j.egypro.2014.11.190

Keywords: Amine Synthesis, Cyclic Amines, Piperidine, Piperazine, Alkanolamines, CO_2 mass transfer

1. Introduction

Post-Combustion Capture of CO_2 (PCC) from coal fired power station flue gas streams using amine based solvent systems currently represents the most technologically mature means of implementing carbon capture and storage (CCS).[1,2] It will be the first technology implemented on a commercial scale/application to reduce CO_2 emissions from coal-fired power stations globally in the near term. However, the application of the technology is still facing several challenges:

- Requisite for more efficient amines to react with CO_2 rapidly and achieve high CO_2 loadings given low CO_2 partial pressures in the gas stream
- Amines must release CO_2 more rapidly and efficiently during desorption with lower overall energy consumption
- Greater stability of amines in the presence of other acidic and oxidative gases, such as NOx, SOx and O_2, which make amine degradation a serious problem during operation
- Long term effects from the treatment of large quantities of flue gases may inflict local environmental issues and impose operational issues (i.e. faults caused by corrosion).

The work presented here aims to provide higher efficiency solvents based on single molecule designer amines in comparison with MEA for post combustion capture of CO_2. These amines combine structural advantages in CO_2 absorption-desorption process to improve energy performance of the solvent while retaining reasonable absorption rates. The study of designer amines here also aims to extend the current knowledge base around the influence of amine structure on the reactions between CO_2 and aqueous amines.

1.1. CO_2 reaction pathways

A brief summary of the reactions occurring in CO_2-amine solutions according to the different amine classes is presented in equations (1) to (4).

Primary and secondary amines react to form carbamates via a fast nucleophilic reaction with CO_2 as described in equation (1).[3] The stability of the carbamate determines the stoichiometry of the reaction which is limited to 0.5 moles of CO_2 absorbed per mole of amine in the case of stable carbamates given the reaction requires a second amine molecule to receive protons released during the formation (of carbamate). Steric hindrance can enhance the conversion of carbamates to bicarbonates resulting in a higher CO_2 capture capacity, but it can also have a negative impact on reaction rates.[4,5]

$$2R_1R_2NH + CO_2 \longleftrightarrow R_1R_2NCO_2^- + R_1R_2NH_2^+ \quad (1)$$

Tertiary amines do not form carbamates, rather they act as a base to accept protons from the slow reaction of CO_2 with H_2O. This scenario is described in equation (2). While the absorption rates associated with this pathway can be a limiting factor, amines which follow this pathway typically result in higher CO_2 loadings and require lower energies during CO_2 desorption. It is therefore desirable to combine the advantages of different amines to make more efficient solvents for CO_2 capture.

$$R_1R_2R_3N + CO_2 + H_2O \longleftrightarrow HCO_3^- + R_1R_2R_3NH^+ \quad (2)$$

The formulation of two or more amine molecules into a single blended solvent is a common method used to combine the optimum properties of individual amines. This scenario is described by equation (3).

$$R_1R_2NH + R_1R_2R_3N + CO_2 \longleftrightarrow R_1R_2NCO_2^- + R_1R_2R_3NH^+ \quad (3)$$

However, while this approach has merit, it also has the limitation that the mixed solvent typically has the volatility, toxicity and stability of the worst component in the formulation. As an alternative to this scenario, the - of two or more amine groups into a single molecule has several inherent advantages, notably the stoichiometric efficiency of the absorption reaction which dictates that only one molecule of amine is required per molecule of CO_2 since the single molecule is performing both the reactive (with CO_2) and proton accepting roles. [6] The scenario for a di-amine is demonstrated in equation (4) where N_1N_2 represents a simple di-amine. The design and synthesis of such amines allows molecular control over the amine properties including steric hindrance, amine type (primary, secondary, tertiary), and functionality, in order to capture the rapid reaction rate of primary and secondary amines as well as fast intra-molecular proton transfer to enhance bicarbonate formation. Therefore, the inherent benefit of these amines is the potential to have larger CO_2 capture capacities than MEA, while ideally maintaining competitive CO_2 mass transfer rates.

$$N_1N_2 + CO_2 \longleftrightarrow N_1H^+N_2CO_2^- \tag{4}$$

2. Experimental section

2.1. Chemicals

The chemicals used in the synthesis of the amines were purchased from Sigma Aldrich, Strem Chemicals and Oakwood chemicals. CO_2 and N_2 gases were purchased from BOC gases (>99%).

2.2. Designer amines

The series of amines proposed in this work are based on two skeletons as shown in Figure 1. The introduction of various substituents on the nitrogen groups was proposed in order to maximize the advantages of different amine types and to improve the amine properties for PCC. The two parent skeleton amines share structural similarities to the sub-family of piperidine derivatives that, as a group of amines, were found to display excellent CO_2 loadings in our previous study.[7] Furthermore, the skeleton amines also have partial structural similarity to piperazine which is widely used as a promoter in amine solvents for CO_2 capture and can be modified with different substituent to improve the properties of the final products. Structural modification of the parent skeleton molecules through selective addition of carbon chains, hydroxyl groups, and additional amine groups, around the cyclic ring structure, was performed here, ultimately giving rise to a series of 30 new amines.

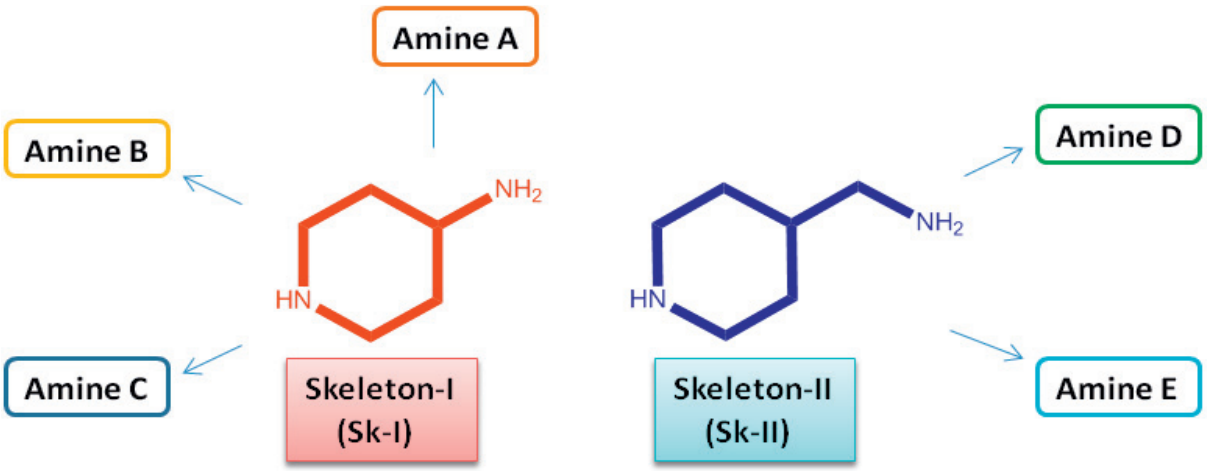

Figure 1. Designer amine synthesis based on parent molecules

2.3. Cyclic capacity analysis via ^{13}C NMR spectroscopy

Thirty three amines, including 30 designer amines, MEA, and the two parent skeleton amines, were studied for their cyclic capacities using quantitative ^{13}C NMR spectroscopy. CO_2 absorption-desorption experiments were conducted using the experimental setup described in previous work.[8,9] This method is highly suited to the investigation of cyclic capacities when the availability of material for testing is limited.

Briefly, a mixed synthetic gas containing 15% CO_2 in N_2 was humidified and bubbled through the aqueous amine solution in a jacketed reaction flask. The temperature of the vessel was maintained by a circulating water bath at 40˚C for absorption, and 90˚C for desorption. The amine solution was exposed to the gas mixture for 18 hours or until it had reached the maximum CO_2 loading as indicated in the NMR spectrum (no further changes). Desorption of CO_2 from the amine solutions was performed at 90˚C for one hour using the same experimental setup.

2.4. Energy performance estimations

To gain insight into the potential benefit of using our designer amines, simple estimations of the energy requirements for desorption of CO_2 were made using the energy balance.[10] The experimental conditions that were used for the measurements were taken as the conditions for the estimation of the energy requirements: designer amine concentration of 2.0 M; 40°C absorption temperature; heating to 90°C desorption temperature; and a total pressure of 101.3 kPa. The enthalpy of CO_2 absorption (desorption is the same value with opposite sign), ΔH_{CO2}, was assumed to be equal to MEA (-85 kJ / mol). These conditions represent suboptimal process conditions and the enthalpy of absorption represents an upper limit as it is a value typical of a primary amine†. The secondary and tertiary amine functional groups in many of the designer amines will have a smaller enthalpy of absorption and will have even better energy performance than that estimated here. The estimated energy performance improvements can be considered conservative estimates, with significant scope for greater improvement through more detailed characterisation of the amine properties, optimisation of process conditions and amine concentration. More experimental data of the CO_2-amine-water vapour-liquid-equilibria of these systems is required to develop more precise estimates, and this is currently not possible with the small amounts of designer amine available.

There are three main terms contributing to the energy requirement of CO_2 desorption (q_{des} (kJ / g) (equation (8)). They are: the heating of the absorbent to desorption temperature (q_{heat} (kJ / g) (equation (5) which is governed by the liquid circulation rate and heat capacity; water evaporation (q_{vap} (kJ / g) (equation (6)) and the energy required to reverse the chemical reactions and to release CO_2 (q_{abs} (kJ / g) (equation (7)).

$$q_{heat} = \frac{C_p (T_{des} - T_{initial})}{\Delta\alpha} \frac{M_{sol}}{M_{CO_2}} \frac{1}{X_{H_2O}} \tag{5}$$

$$q_{vap} = \Delta H_{vap} \frac{p_{H_2O}}{p_{CO_2}} \frac{1}{M_{CO_2}} \tag{6}$$

$$q_{abs} = \frac{\Delta H_{CO_2}}{M_{CO_2}} \tag{7}$$

$$q_{des} = q_{heat} + q_{vap} + q_{abs} \tag{8}$$

In these equations C_p is the heat capacity of the solution (assumed equal to water, 4.18 kJ / g / K), $T_{initial}$ is the initial temperature of the loaded solution (40°C), T_{des} is the desorption temperature to which the solution is heated (90°C), $\Delta\alpha$ is the difference in mass based CO_2 loading (g CO_2 / g solution) between the absorber and desorber temperature, M_{sol} is the molecular mass of the solution (g / mol), M_{CO2} is the molecular mass of CO_2 (44.01 g / mol),

† The magnitude of the enthalpy of absorption varies with the structural features of amine molecules but follows the general trend tertiary amines < secondary amines < primary amines.

X_{H2O} is the mole fraction of water in the solution, ΔH_{vap} is the enthalpy of water vaporisation (-40 kJ / mol), p_{H2O} and p_{CO2} are the partial pressures of water and CO_2 respectively at 90°C ($p_{H2O} = X_{H2O} p^*_{H2O}$ and $p_{CO2} = 101.3 - p_{H2O}$ where p^*_{H2O} is the vapour pressure of pure water, kPa) and ΔH_{CO2} is the enthalpy of CO_2 absorption (-85 kJ / mol).

Aqueous MEA, at 4.0 M, was used as the base for comparison to the performance of the synthesised amines. This concentration was chosen because it yields the same total nitrogen concentration as 2.0M solutions of the di-amines tested. Under the conditions used this gives an energy requirement of 9.34 kJ / g CO_2.

2.5. Wetted wall column

The absorption efficiency of a solvent can be measured in the laboratory using a wetted wall column apparatus that is designed to mimic the gas-liquid contact occurring in typical packed absorption columns. The apparatus operates by counter-currently contacting an amine liquid which is flowing down over an absorption column with a gas stream travelling upwards and adjacent to the liquid before exhausting at the top. Such measurements combine the processes of CO_2 diffusion across the gas-liquid interface, and chemical reaction within the amine liquid acting to consume CO_2, resulting in overall mass transfer co-efficients for CO_2 absorption in each of the amine solutions over a range of CO_2 loading conditions. The absorption of CO_2 into 2.0 M solutions of the designer amines (4.0 N amine concentrations in the case of di-amines and 6.0N for tri-amines) was performed here at 40°C. The apparatus used in this work was similar to that used in our previous studies and details of the setup can be found there.[11] CO_2 absorption into partially CO_2 loaded solutions was performed to gain insight into the performance of the solvent as it would progress through a realistic absorption column. Corresponding measurements in 4.0M MEA solutions over a range of CO_2 loadings was performed for comparison.

3. Results and Discussion

3.1. Cyclic capacity

The obtained cyclic capacity results for the designer amines here are displayed in Figure 2 in terms of a molar and mass basis. The former molar cyclic capacity is defined as moles of CO_2 per mole of nitrogen (rather than moles of amine, as the tested amine may contain different numbers of nitrogen) while mass based cyclic capacity is calculated as the grams of CO_2 per grams of amine. Figure 2 additionally displays the relative cyclic capacity of MEA for comparison.

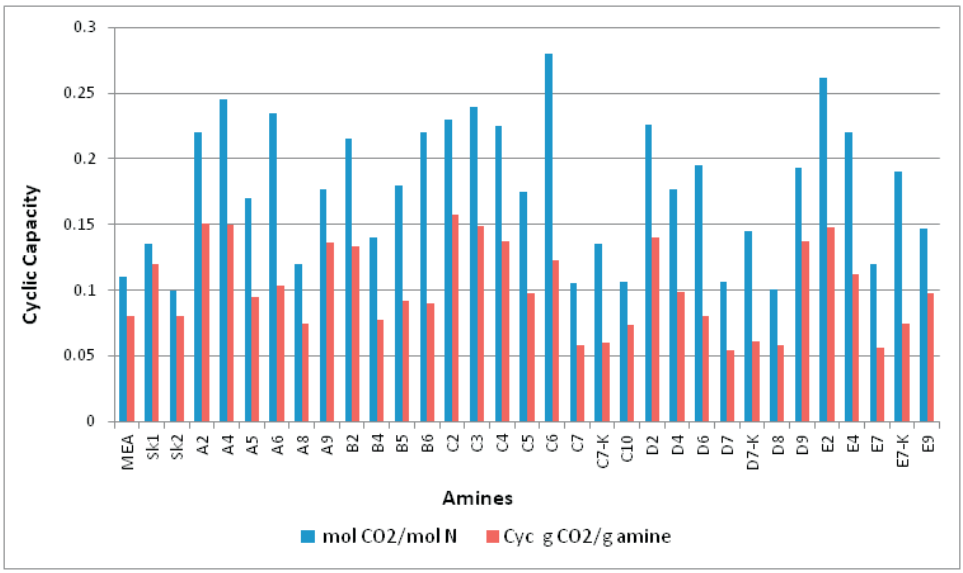

Figure 2. Cyclic capacity of designer amines and MEA

The results in Figure 2 display that 26 amines have increased cyclic capacity compared to MEA on a molar basis indicating that most of the designer amines contain more effective amino-functional groups. Twelve amines obtained more than 80% improvement in cyclic capacity on a molar basis and the largest improvement is 158% for Amine C6. When the molecular weight of the amines are considered, twenty of the designer amines displayed an increased cyclic capacity (mass basis) than MEA while nine of the amines showed an improvement of 70% or more.

3.2. Energy performance estimations

The improvement in the energy estimate for each of the designer amines compared to MEA, calculated using equation 8, is shown in Figure 3. From the figure some ten amines yield improvements above 27% compared to MEA. Amine D9 yields the greatest overall improvement in energy requirement of some 32%. These can be considered the most promising preliminary candidates. With the data currently available for each amine it is effectively the cyclic capacity and the amine molecular mass that define the energy performance. From the simulations it is the q_{heat} term which makes the largest contribution. This term is governed by the changes in cyclic capacity and molecular mass from amine to amine. The larger the cyclic capacity, and the smaller the molecular mass, the smaller the net mass to be heated per unit of CO_2 released.

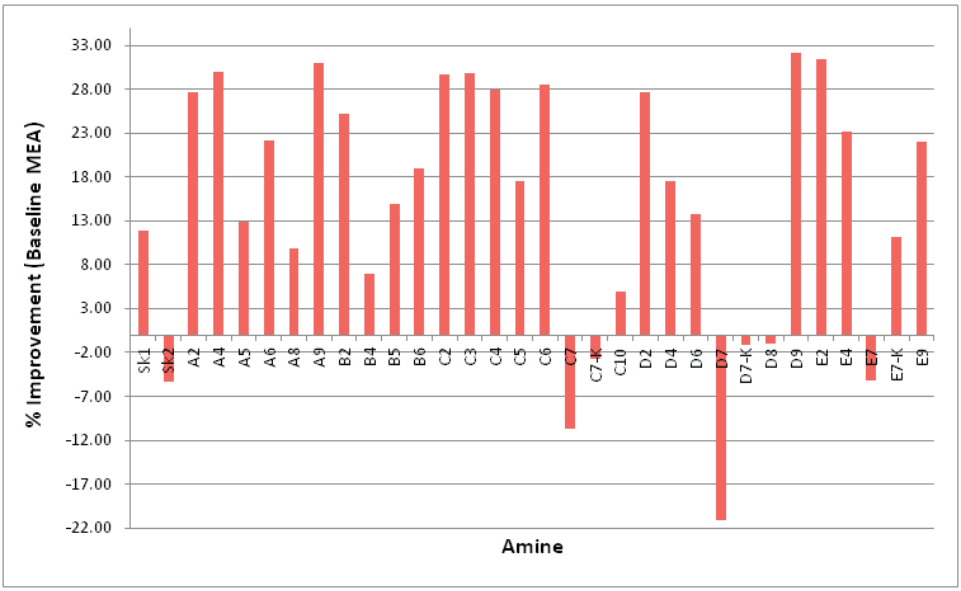

Figure 3. Estimated improvement in energy performance compared to MEA

3.3. Overall mass transfer coefficients

CO_2 absorption rates at 40°C into 2.0 M solutions of the designer amines A4, A9, C3, and C4, and 4.0M MEA for comparison, was investigated in this work using a wetted wall column contactor. The overall mass transfer coefficients, K_G, as a function of CO_2 loading, are presented in Figure 4.

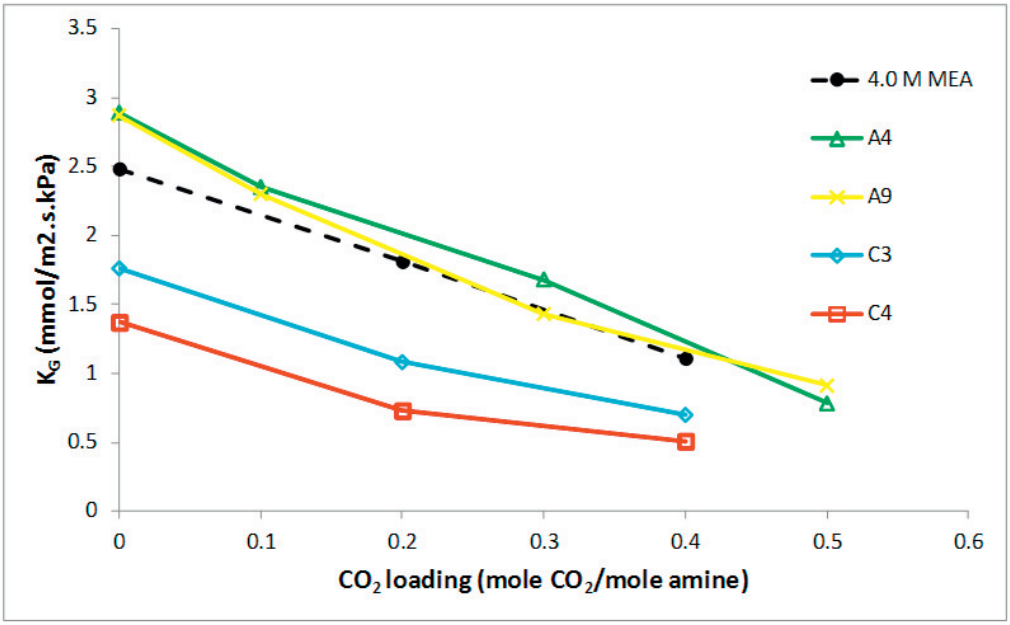

Figure 4. Overall mass transfer co-efficients, K_G, as a function of CO_2 loading in 2.0 M solutions of amines A4, A9, C3, and C4 at 40°C. Data for 4.0 M MEA included for comparison.

From the mass transfer coefficients in Figure 4 the reactivity of the amines follows the trend A4 ~ A9 > MEA > C3 > C4. In all cases here, CO_2 mass transfer decreases linearly with increasing CO_2 loading, which is in line with the supposition of a depletion of the bulk concentration of free "reactive" amine as CO_2 loading increases, and increases in solution viscosity due to the increasing amount, and interactions, of charged species (carbonate, bicarbonate, protonated amine, carbamate etc) in the solution. Both amines A4 and A9 demonstrate mass transfer rates up to 2 times higher than amines C3 and C4 over the entire loading range. Importantly, mass transfer above diffusion is maintained in amines A4 and A9 up to a loading of 0.5, improving the overall working range of the solvent.

Conclusions

Through amine synthesis this work has highlighted a series of designer amines capable of achieving similar or greater capture performance when compared to monoethanolamine (MEA). The combination of larger cyclic capacities, lower estimations of the minimum reboiler duty, and comparable CO_2 mass transfer rates places several of these amines firmly as promising candidates to achieve the largest overall cost reduction (via contributions of the solvent) for a CO_2 capture process.

Acknowledgements

The authors wish to acknowledge financial assistance provided through both CSIRO Energy Flagship and Australian National Low Emissions Coal Research and Development (ANLEC R&D). ANLEC R&D is supported by Australian Coal Association Low Emissions Technology Limited and the Australian Government through the Clean Energy Initiative.

References

[1] Leung, D. Y. C.; Caramanna, G.; Maroto-Valer, M. M. An overview of current status of carbon dioxide capture and storage technologies. *Renewable and Sustainable Energy Reviews* **2014**, *39*, 426-443.
[2] Macdowell, N.; Florin, N.; Buchard, A.; Hallett, J.; Galindo, A.; Jackson, G.; Adjiman, C. S.; Williams, C. K.; Shah, N.; Fennell, P. An Overview of CO_2 Capture Technologies. *Energy and Environmental Science* **2010**, *3*, 1645-1669.
[3] Conway, W.; Wang, X.; Fernandes, D.; Burns, R.; Lawrance, G.; Puxty, G.; Maeder, M. Comprehensive Kinetic and Thermodynamic Study of the Reactions of CO_2(aq) andHCO_3^- with Monoethanolamine (MEA) in Aqueous Solution. *Journal of Physical Chemistry A* **2011**, *115*, 14340–14349.

[4] Hook, R. J. An Investigation of Some Sterically Hindered Amines as Potential Carbon Dioxide Scrubbing Compounds. *Industrial and Engineering Chemistry Research* **1997**, *36*, 1779-1790.
[5] Conway, W.; Wang, X.; Fernandes, D.; Burns, R.; Lawrance, G.; Puxty, G.; Maeder, M. Toward the Understanding of Cheimical Absorption Processes for Post-Combustion Capture of Carbon Dioxide: Electronic and Steric Considerations from the Kinetics of Reactions of CO_2(aq) with Sterically Hindered Amines. *Environmental Science and Technology* **2013**, *47*, 1163-1169.
[6] Conway, W.; Fernandes, D.; Burns, R.; Lawrance, G.; Puxty, G.; Maeder, M. Reactions of CO_2 with Aqueous Piperazine Solutions: Formation and Decomposition of Mono- and Dicarbamic Acids/Carbamates of Piperazine at 25.0 °C. *Journal of Physical Chemistry A* **2013**, *117*, 806-813.
[7] Puxty, G.; Rowland, R.; Allport, A.; Yang, Q.; Bown, M.; Burns, R.; Maeder, M.; Attalla, M. Carbon Dioxide Postcombustion Capture: A Novel Screening Study of the Carbon Dioxide Absorption Performance of 76 Amines. *Environmental Science and Technology* **2009**, *43*, 6427-6433.
[8] Yang, Q.; Bown, M.; Abdelselam, A.; Winkler, D.; Puxty, G.; Attalla, M. A Carbon-13 NMR Study of Carbon Dioxide Absorption and Desorption with Aqueous Amine Solutions. *Energy Procedia* **2009**, *1*, 955-962.
[9] Ballard, M.; Bown, M.; James, S.; Yang, Q. NMR studies of mixed amines. *Energy Procedia* **2011**, *4*, 291-298.
[10] Oexmann, J.; Kather, A. Minimising the Regeneration Heat Duty of Post-combustion CO_2 Capture by Wet Chemical Absorption: The Misguided Focus on Low Heat of Absorption Solvents. *International Journal of Greenhouse Gas Control* **2010**, *4*, 36-43.
[11] Puxty, G.; Rowland, R.; Attalla, M. Comparison of the Rate of CO_2 Absorption into Aqueous Ammonia and Monoethanolamine. *Chemical Engineering Science* **2010**, *65*, 915-922.